KC-1a : a certified reference ore (84-6E)

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KC-Ia: A CERTIFIED REFERENCE ORE

H.F. STEGER AND W.S. BOWMAN

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KC-1a: A CERTIFIED REFERENCE ORE

by

H.F. Steger* and W.S. Bowman**

SYNOPSIS

A 276 kg sample of a base metal ore from Timmins, Ontario, has been prepared as a compositional reference material to replace the similar certified ore, KC-1, the stock of which has been exhausted. KC-1a was ground to minus 74 µm and mixed in one lot. Approximately one half of this ore was bottled in 200 g units and tested for homogeneity with respect to its zinc and silver contents by chemical methods. The remaining material is being stored in bulk under periodic purging with nitrogen gas.

In a "free choice" analytical program, 19 laboratories contributed results for one or more of zinc, lead, copper, tin and silver in one bottle of KC-1a. Based on a statistical analysis of the data, the following recommended values were assigned: Zn, 34.65%; Pb, 2.24%; Cu, 0.63%; Sn, 0.61%; and Ag, 0.167%.

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Note: Major contributions were also made by other staff members of the Mineral Sciences Laboratories.

KC-1a: MINERAI DE RÉFÉRENCE

par

H.F. Steger* et W.S. Bowman**

SYNOPSIS

Un échantillon de 276 kg de minerai de métaux communs provenant de Timmins en Ontario a été préparé comme matériau de référence de composition pour remplacer le minerai certifié analogue, KC-1, dont l'inventaire avait été épuisé. Le KC-1a a été broyé à une granulométrie de moins 74 µm et mélangé en lot de minerai. Approximativement une moitié de ce minerai a été embouteillée en unités de 200 g et soumise à des essais d'homogénéité quant au zinc et à l'argent par des méthodes chimiques. Le reste du matériau se met en réserve en gros avec une purge périodique avec du gaz d'azote.

En vertu d'un programme analytique de "libre choix", 19 laboratoires ont soumis les résultats pour un ou plusieurs des éléments suivants: zinc, plomb, cuivre, étain et argent sur une bouteille du KC-1a. Suite à l'analyse statistique des données, les valeurs recommandées suivantes ont été assignées: Zn, 34,65%; Pb, 2,24%; Cu, 0,63%; Sn, 0,61%; et Ag, 0,167%.

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Nota: D'autres membres du personnel des Laboratoires des sciences minérales ont également apporté une grande contribution à ce projet.

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INTRODUCTION

The preparation, characterization and certification of base metal ore KC-1a is a further contribution of the Canadian Certified Reference Materials Project (CCRMP) in its endeavour to provide compositional reference ores, concentrates and related products typical of Canadian deposits and generally unavailable from other sources for use in analytical laboratories associated with mining, metallurgy and the earth sciences. Other certified reference materials are described in a catalogue available from CANMET, Energy, Mines and Resources, Ottawa, Canada (1).

KC-1a is intended to replace KC-1, the supply of which was exhausted (2,3). KC-1 which was certified in 1974 for zinc, lead, copper, tin and silver had been a popular reference material because of the large number of certified elements and because of its mineralogical complexity.

An interlaboratory program was conducted to obtain results for 5 elements from 19 commercial, industrial and government laboratories using analytical methods of their choice. The results should therefore be indicative of the practical state-of-the-art of the analysis for these elements.

NATURE AND PREPARATION

The raw material for KC-1a was hand-picked by Dr. D. Scott of Kidd Creek Mines Ltd. and donated to CCRMP in August 1983. The mineralogy of ore from the Kidd Creek deposit has been described in detail by Petruk and Owens (4). Briefly, the ore is from a zone of massive sphalerite-pyrite containing native silver and galena.

The raw material was dry-ground in September 1983 to pass a 74 µm screen. The powdered ore weighing 276 kg was tumbled in a 570 L conical blender for 14 h. Approximately one half of the blended material was bottled in 200 g units which were heat-sealed in polyester - aluminium foil - polyethylene pouches to prevent oxidation while in storage at CANMET. The remainder of the material is being stored in bulk under periodic purging with nitrogen gas.

The analysis of 15 randomly selected bottles of KC-1a for both zinc and silver demonstrated the material to be sufficiently homogeneous for use as a reference material. The results of the evaluation of the homogeneity of KC-1a are reported in Appendix A.

The approximate mineralogical composition for the major constituents in KC-1a is given in Table 1. Siderite, pyrrhotite, tetrahedrite + stephanite, feldspar and chlorite are also present in minor amounts. The chemical composition and particle size analysis are given in Tables 2 and 3.

Table 1 - Approximate mineralogical composition

Mineral	Mass %
Sphalerite	51.7
Quartz	21.4
Pyrite	17.1
Galena	2.6
Chalcopyrite	1.8
Cassiterite	0.8
Silver	0.16
Carbon	0.02

Table 2 - Approximate chemical composition

Element	Mass %*
Zn	34.7
S	27.5
Fe	10.9
Si	10.4
Pb	2.3
Cu	0.6
Sn	0.6
Ag	0.16
C (total)	0.02
Al	0.10
Mn	0.01
H_2O (105°C)	0.09

*Mean of a minimum of two determinations.

Table 3 - Particle size analysis (wet screen)

Size of fraction (μm)	wt %
-104 + 74	0.0
-74 + 46	11.8
-46 + 37	11.6
-37	76.6

INTERLABORATORY PROGRAM FOR CERTIFICATION

The laboratories that participated in the certification program are listed in Appendix B. Each was assigned a code number which bears no relation to its alphabetical order. The results from CANMET are reported openly.

Table 4 - Recommended values and statistical parameters (outliers excluded)

Element	No. of laboratories	No. of sets of results	No. of results	Overall mean	95% CL Low	95% CL High	σ_A*
				wt %			
Zn	15	20	100	34.65	34.51	34.80	0.16
Pb	18	22	110	2.24	2.21	2.27	0.02
Cu	18	23	114	0.629	0.614	0.644	0.006
Sn	16	18	90	0.61	0.59	0.63	0.01
Ag	18	24	120	0.167	0.165	0.169	0.002

Table 5a - Summary of analytical methodology for zinc (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption spectrometry	One or more of HCl + HNO_3 + HF + $HClO_4$ + H_2SO_4	9, 14, 16a, 17b	20	34.33
Titrimetry	One or more of HCl + HNO_3 + HF + $HClO_4$ + Br_2; Zn separated by extraction into MIBK as thiocyanate; stripped and titrated with EDTA	CANMET, 6a, 15, 16b	20	34.79
	One or more of HCl + HNO_3 + HF + $HClO_4$; R_2O_3 separated by precipitation; Zn titrated with EDTA	1a, 1b, 2, 8, 10	25	34.50
	One or more of HCl + HNO_3 + HF + H_2SO_4; R_2O_3 separated by precipitation; Zn titrated with ferrocyanide	4, 13	10	34.85
ICP-AES	One or more of HCl + HNO_3 + HF + $HClO_4$	18b	5	35.17
	Na_2O_2 fusion; taken up in dilute HCl	6b	5	34.82
Xrf	$K_2S_2O_7$ fusion; ground and pelletized	5	5	34.81
	No details	17a	5	34.31
Polarography	$HClO_4$	18a	5	35.28

Each laboratory was requested to contribute five replicate results for zinc, lead, copper, tin and silver for one bottle of KC-1a by methods of its own choice and to report the results on an "as is" basis. Some laboratories however deviated from the request for five results for an element or contributed results for more than five elements. When a laboratory submitted results by more than one method for an element, each set was considered statistically independent.

The recommended values for KC-1a are presented in Table 4. Methodological and analytical information is presented in Tables 5a through 6e.

STATISTICAL TREATMENT OF ANALYTICAL RESULTS

DETECTION OF OUTLIERS

Any sets of results obviously suspect for methodological reasons were rejected. Also, the sets of results whose means differed by more than twice the overall standard deviation from the initially calculated mean value were not used in subsequent computations to avoid biasing of the statistics. All results that were rejected are identified in Tables 6a through 6e.

Table 5b - Summary of analytical methodology for lead (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption spectrometry	One or more of HCl + HNO_3 + HF + $HClO_4$	1, 2, 3, 4, 8, 9, 10, 11, 12, 13, 14, 15, 16, 18a	70	2.25
	HCl + HNO_3 + HF + $HClO_4$; Sn, As volatilized with Br_2; Pb separated by co-precipitation as hydrous oxide; dissolved in HNO_3	CANMET (a)	5	2.25
	HCl + HNO_3 + HF + $HClO_4$; Sn, As volatilized with Br_2	CANMET (b)	5	2.28
	Na_2O_2 fusion; dissolved in HCl + HNO_3	6c	5	2.14
ICP-AES	One or more of HCl + HNO_3 + HF + $HClO_4$	7, 18b	10	2.19
	Na_2O_2 fusion; dissolved in HCl	6b	5	2.14
Titrimetry	Acid decomposition; Pb precipitated as CrO_4^{2-}; dissolved and titrated with $Na_2S_2O_3$	6a	5	2.28
Xrf	$K_2S_2O_7$ fusion; ground and pelletized	5	5	2.31

Table 5c - Summary of analytical methodology for copper (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption spectrometry	One or more of HCl + HNO_3 + HF + $HClO_4$	1, 2a, 3, 4, 8, 9, 10, 11, 12, 13, 15, 16, 17, 18b	69	0.626
	HCl + HNO_3 + HF + $HClO_4$; Sn, As volatilized with Br_2	CANMET	5	0.630
	Na_2O_2 fusion; dissolved in HCl + HNO_3	6c	5	0.606
ICP-AES	One or more of HCl + HNO_3 + HF + $HClO_4$	7, 18c	10	0.635
	Na_2O_2 fusion; dissolved in HCl	6b	5	0.588
Titrimetry	Classical long iodide method	2b	5	0.652
Colorimetry	Acid decomposition; Cu reacted with cuproine	6a	5	0.608
Xrf	$K_2S_2O_7$ fusion; ground and pelletized	5	5	0.641
Polarography	$HClO_4$	18a	5	0.702

Table 5d - Summary of analytical methodology for tin (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption spectrometry	Na_2O_2 or Na_2O_2 + Na_2CO_3 fusion	2, 4, 11, 13, 15, 16, 17	35	0.602
	Na_2O_2 fusion; Si driven off with HF; Sn separated as iodide by extraction into toluene; stripped with H_2SO_4 + HCl	CANMET	5	0.599
	$Li_2B_4O_7$ fusion; dissolved in HNO_3	8	5	0.676
	Roasted; NaOH fusion; dissolved in HCl; SnH_4 generation into quartz tube	9	5	0.638
ICP-AES	Na_2O_2 or Na_2O_2 + NaOH or Na_2O_2 + Na_2CO_3 fusion; dissolved in HCl	6b, 7, 18a	15	0.570
Xrf	2:1 sample:sand + binder; pelletized	5	5	0.669
	No details	10, 12	10	0.665
Titrimetry	Na_2O_2 + NaOH or Na_2O_2 + Na_2CO_3 fusion; reduced with Pb, iodate titration	6a, 18b	10	0.577

Table 5e - Summary of analytical methodology for silver (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Fire assay-gravimetry	Fire assay-lead button collection; cupellation; bead weighed	1a, 1b, 2, 3, 4, 5b, 13, 15b, 17, 18c	50	0.165
Atomic absorption spectrometry	One or more of HCl + HNO_3 + $HClO_4$ + HF + H_2SO_4 + Br_2; taken to dryness; dissolved in one or both of HCl + HNO_3	CANMET 8, 9, 10, 11, 14, 15a, 16, 18a, 18b	50	0.169
	Na_2O_2 fusion; dissolved in HCl + HNO_3	6b	5	0.164
ICP-AES	One or more of HCl + HNO_3 + HF + $HClO_4$	7	5	0.168
	Na_2O_2 fusion; dissolved in HCl	6a	5	0.155
Xrf	Loose powder	5a	5	0.174

Table 6a - Analytical results, laboratory means and standard deviations for zinc

ZINC WT %

						MEAN	S.D.
LAB- 1 (TITR)	34.59	34.51	34.60	34.56	34.58	34.5680	.0356
LAB- 1 (TITR)	34.50	34.52	34.52	34.47	34.46	34.4940	.0279
LAB- 2 (TITR)	34.54	34.49	34.59	34.54	34.64	34.5600	.0570
LAB- 3 (AA)	35.90	35.70	35.80	35.70	35.80	35.7800	.0837
LAB- 4 (TITR)	34.60	34.70	34.60	34.70	34.80	34.6800	.0837
LAB- 5 (XRF)	34.81	34.87	34.80	34.83	34.75	34.8120	.0438
LAB- 6 (TITR)	34.85	34.93	34.93	34.85	35.08	34.9280	.0939
LAB- 6 (ICP)	34.65	34.81	34.96	34.92	34.77	34.8220	.1236
LAB- 7 (ICP)	33.30	33.10	32.70	34.00	32.50	33.1200	.5848
LAB- 8 (TITR)	34.50	34.19	34.21	34.37	34.50	34.3540	.1504
LAB- 9 (AA)	33.9	33.9	34.4	33.9	34.2	34.0600	.2302
LAB-10 (TITR)	34.59	34.54	34.52	34.52	34.51	34.5360	.0321
LAB-12 (AA)	32.0	32.2	32.1	31.8	31.9	32.0000	.1581
LAB-13 (TITR)	34.97	35.07	34.97	35.07	34.97	35.0100	.0548
LAB-14 (AA)	34.7	34.9	34.3	35.3	33.3	34.5000	.7616
LAB-15 (TITR)	34.92	34.91	34.94	34.94	34.94	34.9300	.0141
LAB-16 (AA)	33.84	34.37	34.68	34.54	34.11	34.3080	.3370
LAB-16 (TITR)	34.77	34.71	34.84	34.66	34.77	34.7500	.0682
LAB-17 (XRF)	34.17	34.17	34.32	34.45	34.44	34.3100	.1377
LAB-17 (AA)	34.64	34.58	34.43	34.29	34.31	34.4500	.1570
LAB-18 (POLAR)	35.42	35.22	35.25	35.08	35.41	35.2760	.1422
LAB-18 (ICP)	35.59	34.58	35.00	34.86	35.81	35.1680	.5146
CANMET (TITR)	34.52	34.48	34.62	34.54	34.62	34.5560	.0623

Table 6b - Analytical results, laboratory means and standard deviations for lead

LEAD WT %

						MEAN	S.D.
LAB- 1 (AA)	2.28	2.30	2.26	2.28	2.28	2.2800	.0141
LAB- 2 (AA)	2.21	2.21	2.21	2.21	2.21	2.2100	.0000
LAB- 3 (AA)	2.26	2.27	2.26	2.25	2.27	2.2620	.0084
LAB- 4 (AA)	2.40	2.37	2.40	2.38	2.40	2.3900	.0141
LAB- 5 (XRF)	2.284	2.362	2.336	2.301	2.291	2.3148	.0331
LAB- 6 (TITR)	2.26	2.28	2.31	2.26	2.29	2.2800	.0212
LAB- 6 (ICP)	2.12	2.17	2.15	2.14	2.12	2.1400	.0212
LAB- 6 (AA)	2.13	2.13	2.15	2.16	2.12	2.1380	.0164
LAB- 7 (ICP)	2.12	2.09	2.18	2.08	2.08	2.1100	.0424
LAB- 8 (AA)	2.18	2.21	2.21	2.21	2.25	2.2120	.0249
LAB- 9 (AA)	2.22	2.26	2.20	2.26	2.22	2.2320	.0268
LAB-10 (AA)	2.272	2.272	2.285	2.285	2.262	2.2752	.0098
LAB-11 (AA)	2.27	2.28	2.28	2.28	2.26	2.2740	.0089
LAB-12 (AA)	2.20	2.10	2.20	2.20	2.20	2.1800	.0447
LAB-13 (AA)	2.27	2.26	2.28	2.26	2.25	2.2640	.0114
LAB-14 (AA)	2.15	2.15	2.17	2.20	2.20	2.1740	.0251
LAB-15 (AA)	2.23	2.24	2.25	2.24	2.23	2.2380	.0084
LAB-16 (AA)	2.21	2.19	2.20	2.19	2.18	2.1940	.0114
LAB-17 (AA)	2.41	2.40	2.39	2.41	2.40	2.4020	.0084
LAB-18 (AA)	2.28	2.30	2.30	2.28	2.28	2.2880	.0110
LAB-18 (ICP)	2.29	2.22	2.21	2.27	2.36	2.2700	.0604
CANMET (AA)	2.256	2.262	2.234	2.250	2.244	2.2492	.0108
CANMET (AA)	2.279	2.303	2.269	2.254	2.275	2.2760	.0178

Table 6c - Analytical results, laboratory means and standard deviations for copper

COPPER WT %

						MEAN	S.D.
LAB- 1 (AA)	0.58	0.56	0.57	0.56	0.58	.5700	.0100
LAB- 2 (AA)	0.65	0.65	0.65	0.66	0.66	.6540	.0055
LAB- 2 (TITR)	0.64	0.64	0.64	0.67	0.67	.6520	.0164
LAB- 3 (AA)	0.65	0.65	0.64	0.64	0.65	.6460	.0055
LAB- 4 (AA)	0.640	0.630	0.630	0.630	0.640	.6340	.0055
LAB- 5 (XRF)	0.642	0.625	0.660	0.632	0.645	.6408	.0134
LAB- 6 (COLOR)	0.61	0.61	0.60	0.61	0.61	.6080	.0045
LAB- 6 (ICP)	0.586	0.588	0.588	0.591	0.587	.5880	.0019
LAB- 6 (AA)	0.607	0.608	0.61	0.606	0.601	.6064	.0034
LAB- 7 (ICP)	0.598	0.602	0.598	0.588	0.586	.5944	.0070
LAB- 8 (AA)	0.634	0.638	0.641	0.642	0.640	.6390	.0032
LAB- 9 (AA)	0.6257	0.6257	0.6231	0.6231	0.6205	.6236	.0022
LAB-10 (AA)	0.650	0.650	0.650	0.650	0.647	.6494	.0013
LAB-11 (AA)	0.623	0.622	0.630	0.632	0.622	.6258	.0048
LAB-12 (AA)	0.60	0.59	0.58	0.58	0.58	.5860	.0089
LAB-13 (AA)	0.56	0.58	0.57	0.58	0.59	.5760	.0114
LAB-14 (AA)	0.51	0.48	0.48	0.47	0.48	.4840	.0152
LAB-15 (AA)	0.630	0.630	0.620	0.630	0.620	.6260	.0055
LAB-16 (AA)	0.607	0.615	0.613	0.615	0.609	.6118	.0036
LAB-17 (AA)	0.642	0.642	0.640	0.643	0.642	.6418	.0011
LAB-18 (POLAR)	0.71	0.70	0.70	0.69	0.71	.7020	.0084
LAB-18 (AA)	0.70	0.70	0.74	0.69	0.69	.7040	.0207
LAB-18 (ICP)	0.68	0.67	0.66	0.68	0.69	.6760	.0114
CANMET (AA)	0.629	0.634	0.630	0.629	0.629	.6302	.0022

Table 6d - Analytical results, laboratory means and standard deviations for tin

TIN WT %

						MEAN	S.D.
LAB- 1 (XRF)	0.81	0.83	0.82	0.81	0.81	.8160	.0089
LAB- 2 (AA)	0.60	0.61	0.61	0.60	0.60	.6040	.0055
LAB- 4 (AA)	0.596	0.606	0.603	0.606	0.601	.6024	.0042
LAB- 5 (XRF)	0.676	0.656	0.680	0.676	0.656	.6688	.0118
LAB- 6 (TITR)	0.60	0.61	0.60	0.59	0.60	.6000	.0071
LAB- 6 (ICP)	0.584	0.586	0.588	0.584	0.581	.5846	.0026
LAB- 7 (ICP)	0.554	0.562	0.568	0.564	0.580	.5656	.0095
LAB- 8 (AA)	0.648	0.646	0.678	0.683	0.724	.6758	.0318
LAB- 9 (AA)	0.66	0.62	0.65	0.63	0.63	.6380	.0164
LAB-10 (XRF)	0.66	0.66	0.66	0.67	0.65	.6600	.0071
LAB-11 (AA)	0.57	0.56	0.60	0.58	0.57	.5760	.0152
LAB-12 (XRF)	0.68	0.66	0.66	0.67	0.68	.6700	.0100
LAB-13 (AA)	0.60	0.59	0.60	0.59	0.60	.5960	.0055
LAB-14 (TITR)	0.80	0.89	0.82	0.86	0.83	.8400	.0354
LAB-15 (AA)	0.598	0.608	0.599	0.600	0.600	.6010	.0040
LAB-16 (AA)	0.623	0.628	0.627	0.643	0.622	.6286	.0084
LAB-17 (AA)	0.609	0.610	0.604	0.612	0.609	.6088	.0029
LAB-18 (ICP)	0.57	0.54	0.525	0.59	0.58	.5610	.0275
LAB-18 (TITR)	0.53	0.55	0.51	0.57	0.61	.5540	.0385
CANMET (AA)	0.597	0.600	0.599	0.604	0.597	.5994	.0029

Table 6e - Analytical results, laboratory means and standard deviations for silver

SILVER WT %

						MEAN	S.D.
LAB- 1 (FA-G)	0.165	0.165	0.165	0.165	0.165	.1650	.0000
LAB- 1 (FA-G)	0.158	0.156	0.162	0.153	0.157	.1572	.0033
LAB- 2 (FA-G)	0.167	0.166	0.167	0.167	0.169	.1676	.0009
LAB- 3 (FA-G)	0.156	0.156	0.155	0.159	0.158	.1568	.0016
LAB- 4 (FA-G)	0.168	0.172	0.171	0.169	0.167	.1694	.0021
LAB- 5 (XRF)	0.176	0.173	0.175	0.173	0.174	.1742	.0013
LAB- 5 (FA-G)	0.170	0.169	0.171	0.171	0.168	.1698	.0013
LAB- 6 (ICP)	0.155	0.157	0.154	0.155	0.156	.1554	.0011
LAB- 6 (AA)	0.168	0.164	0.156	0.166	0.166	.1644	.0038
LAB- 7 (ICP)	0.173	0.166	0.170	0.163	0.166	.1680	.0038
LAB- 8 (AA)	0.159	0.152	0.157	0.159	0.163	.1580	.0040
LAB- 9 (AA)	0.161	0.166	0.168	0.169	0.166	.1660	.0031
LAB-10 (AA)	0.170	0.171	0.170	0.172	0.171	.1708	.0008
LAB-11 (AA)	0.180	0.178	0.177	0.178	0.178	.1782	.0011
LAB-12 (AA)	0.18	0.18	0.19	0.19	0.18	.1840	.0055
LAB-13 (FA-G)	0.165	0.165	0.166	0.166	0.166	.1656	.0005
LAB-14 (AA)	0.180	0.177	0.177	0.177	0.175	.1772	.0018
LAB-15 (AA)	0.1640	0.1639	0.1659	0.1680	0.1640	.1652	.0018
LAB-15 (FA-G)	0.16579	0.16550	0.16537	0.16749	0.16557	.1659	.0009
LAB-16 (AA)	0.169	0.169	0.171	0.171	0.168	.1696	.0013
LAB-17 (FA-G)	0.169	0.170	0.166	0.168	0.169	.1688	.0008
LAB-18 (AA)	0.1707	0.1699	0.1728	0.1708	0.1699	.1708	.0012
LAB-18 (AA)	0.1695	0.1696	0.1692	0.1687	0.1687	.1691	.0004
LAB-18 (FA-G)	0.1697	0.1680	0.1701	0.1677	0.1681	.1687	.0011
CANMET (AA)	0.166	0.166	0.165	0.165	0.167	.1662	.0013

ESTIMATION OF CONSENSUS VALUES AND 95% CONFIDENCE LIMITS

A one-way analysis of variance technique was used to estimate the consensus value and variance. This approach considers the results of the described certification program to be only one sampling out of a universal set of results. The analytical data were assumed to fit the model (5).

$$x_{ij} = \mu + y_i + e_{ij}$$

where x_{ij} = the j^{th} result in set i,

μ = the true consensus value,

y_i = the discrepancy between the mean of the results in the set i ($\bar{x}_i.$) and μ, and

e_{ij} = the discrepancy between x_{ij} and $\bar{x}_i$.

It is assumed that both y_i and e_{ij} are normally distributed with means of zero and variances of ω^2 and σ^2, respectively. The significance of ω^2 is detected by comparing the ratio of between-set mean squares to within-set mean squares with the F statistic at the 95% confidence level and with the appropriate degrees of freedom.

The consensus value of the assumed model is estimated by the overall mean $\bar{x}..$ by:

$$\bar{x}.. = \sum_{i}^{k} \sum_{j}^{n_i} x_{ij} \Big/ \sum_{i}^{k} n_i$$

where n_i = the number of results in set i, and

k = the number of sets.

The value of σ^2 is estimated by s_1^2 which is given by

$$s_1^2 = \sum_{i}^{k} \sum_{j}^{n_i} (x_{ij} - \bar{x}_i.)^2 \Big/ \sum_{i}^{k} n_i - k.$$

The value of ω^2 is estimated by

$$\omega^2 = (s_2^2 - s_1^2) \Big/ \frac{1}{k-1}\left(\sum_i^k n_i - \sum_i^k n_i^2 \Big/ \sum_i^k n_i\right)$$

where

$$s_2^2 = \sum_i^k n_i (\bar{x}_{i\cdot} - \bar{x}_{\cdot\cdot})^2 \Big/ k-1.$$

The variance of the overall mean is given by

$$V[\bar{x}_{\cdot\cdot}] = \left(\sum_i^k n_i^2 / (\sum_i^k n_i)^2\right)\omega^2 + \left(1/\sum_i^k n_i\right)\sigma^2$$

and the 95% confidence limits for $\bar{x}_{\cdot\cdot}$ are

$$\bar{x}_{\cdot\cdot} \pm t_{0.975,\,(k-1)}\sqrt{V[\bar{x}_{\cdot\cdot}]}.$$

The results of the testing of the homogeneity of KC-1a were included. However, to avoid giving an unduly heavy weighting to the contribution for zinc and silver, only five results for each were selected at random out of the 45 available from the evaluation of the homogeneity of KC-1a.

It should be noted that 95% confidence limits denote that if the certification program were performed 100 times, the overall mean in 95 would fall within the prescribed limits.

The average within-set standard deviation, σ_A, is a measure of the average within-bottle precision as determined by the analytical methods used. The implication exists therefore that a laboratory using a method of average or better reproducibility should obtain individual results for a given certified element with a precision that is at least comparable to the reported value of σ_A.

CRITERION FOR CERTIFICATION

The ratio of the between-laboratory to the within-laboratory standard deviation, σ_B/σ_A, where

$$\sigma_B = \sqrt{\left[\sum_i^k \left(\bar{x}_{i\cdot} - (\sum_i^k \bar{x}_{i\cdot})/k\right)\right]^2 \Big/ k-1}$$

is a measure of the quality of the certification data for the reference materials of CCRMP (6). The acceptable upper limit for σ_B/σ_A is 3 for all elements except uranium for which an upper limit of 2 is more realistic.

The criterion for the certification of an element in a reference material is RP, the percentage of sets of results that must be rejected to give a value of σ_B/σ_A equal to or less than the acceptable upper limit. RP should not exceed 15%.

The values of σ_B/σ_A and RP for KC-1a are reported in Table 7.

Table 7 - Values of σ_B/σ_A and RP for KC-1a

Element	σ_B/σ_A	RP	S_{rc}	S_{Lc}
Zn	2.94	4.3	0.24	0.29
Pb	2.65	8.7	0.025	0.064
Cu	3.00	37.5	0.0075	0.034
Sn	2.74	25.0	0.016	0.038
Ag	2.84	12.0	0.0020	0.0057

DISCUSSION

Table 5 is a summary of a methodological classification of accepted analytical results where there is a clear-cut distinction between types of methods in decomposition, separations and determination steps. No attempt was made for any element to detect a statistically significant difference between the overall means of the more popular methods because there was generally not a sufficient number to warrant the test.

The values of RP for copper and tin indicate that the mean values of these elements cannot be certified. CCRMP however is sufficiently confident in these values to give them recommended value status. It is considered that if the quality of the results of the interlaboratory program had been better, the uncertainty in the mean values would be smaller but likely there would be no significant change in the mean values themselves for the following reason.

Steger and Bowman have recently proposed a new procedure for the identification of consensus between laboratories participating in interlaboratory programs (7). Herein, concentration intervals $10\sigma_A$ wide are generated and the number of laboratories whose mean falls in each interval are counted. The interval embracing the largest number of laboratories is assumed to identify that cluster of laboratories displaying maximum consensus. The mean value and associated statistical parameters of these laboratories are accepted to be the best estimate of these quantities. This approach to identify such clusters of consensus was derived for application to interlaboratory programs for which the results were less than ideal, i.e., poor consensus or skewed distribution. This approach, when applied to interlaboratory program results that display normal distribution, should give rise to statistical parameters of essentially the same value as found by analysis of the variance of all results. A comparison of Tables 4 and 8 illustrates that this is indeed the case for all five elements in KC-1a. It can be concluded therefore that the mean values for the elements are very good estimates of the true values. For copper and tin, the addition of more values may reduce the uncertainty in the mean value to make these elements certifiable but it is unlikely to change significantly the current mean values. The previous experience by CCRMP with sodium and potassium in iron ore SCH-1 illustrated this fact (8).

Table 8 - Mean values after consensus identification

Element	Interval wt %	No. of sets of results	Mean value wt %	95% CL
Zn	34.06 - 35.62	20	34.65	0.14
Pb	2.11 - 2.35	21	2.23	0.03
Cu	0.594 - 0.656	16	0.630	0.009
Sn	0.561 - 0.670	16	0.61	0.02
Ag	0.155 - 0.173	21	0.166	0.002

Figures 1a through 1e show the histograms for the five elements in KC-1a and demonstrate good consensus in the interlaboratory programs discussed above.

Laboratory 10 analyzed KC-1a for cadmium in quintuplicate and this value is reported here for information purposes only.

Mean value	0.742% Cd
Standard deviation	0.0045% Cd
No. of results	5

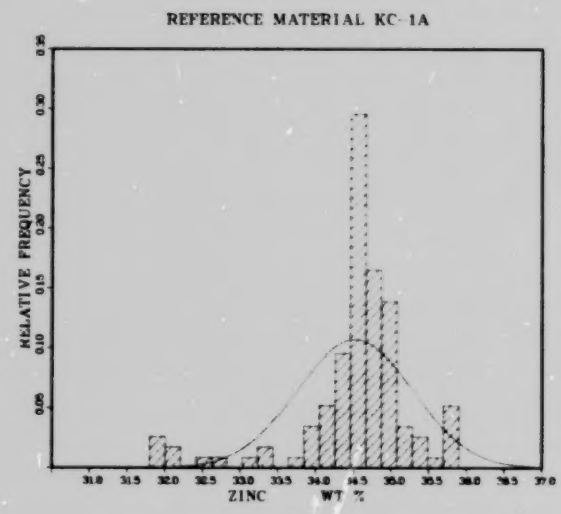

Fig. 1a - Histogram for zinc

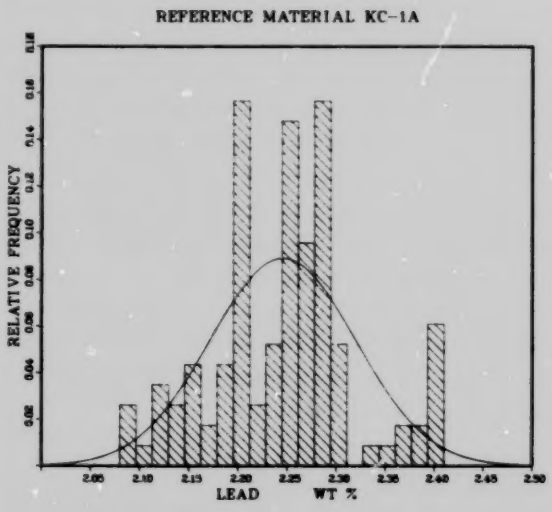

Fig. 1b - Histogram for lead

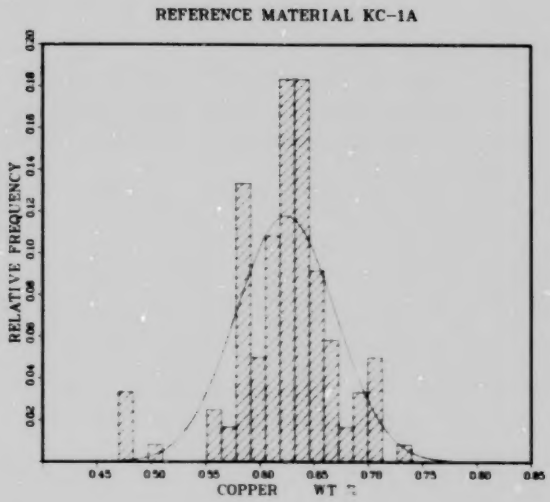

Fig. 1c - Histogram for copper

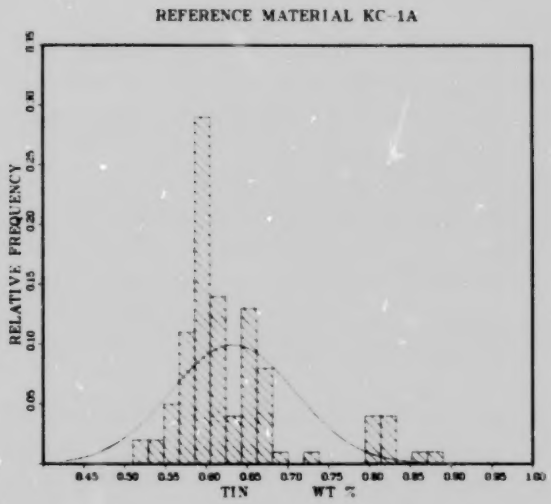

Fig. 1d - Histogram for tin

PROCEDURE FOR CHECKING AN ANALYTICAL METHOD USING KC-1a (9)

Perform n replicate determinations (from separate sub-samples) using the analytical method that is being tested. It is suggested that n = 10 for a one-time investigation. For a periodic check of accuracy of an analytical method, n = 2 for each period is sufficient; however the total number of replicates should be greater than 10.

Compute the following statistics

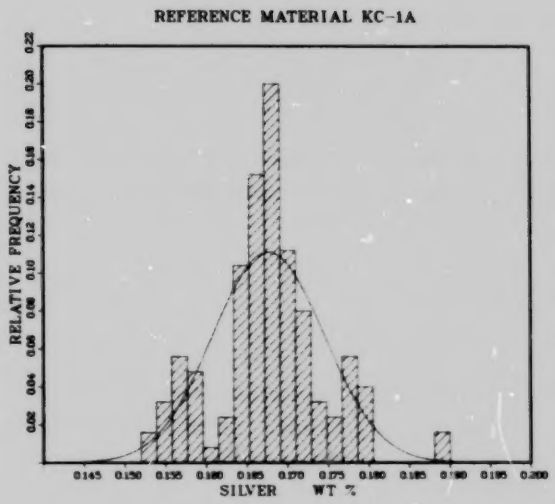

Fig. 1e - Histogram for silver

$$\bar{X} = \sum_{i=1}^{n} X_i / n \quad \text{- mean}$$

$$S_w = \sqrt{\sum_{i=1}^{n} (x_i - \bar{X})^2 \Big/ n-1} \quad \text{- estimated within-laboratory standard deviation i.e., precision of the method}$$

n is the number of analytical results remaining after rejection of outliers.

a) Verification of precision

Compute

$$F = \frac{(S_w)^2}{(S_{rc})^2}$$ where values of S_{rc} for KC-1a, the within-laboratories standard deviation, are given in Table 7.

Compare F against $F_o = F_{0.95,\ n-1,\ DF_c}$ is obtainable from any statistics book. If the degree of freedom DF_c is not given in the certificate, use $DF_c = 60$.

$F \leq F_o$: the analytical method is sufficiently precise

$F > F_o$: the analytical method is not as precise as those used for certification of RM

b) Verification of accuracy

$$\text{If } \left| \bar{X} - A_c \right| \leq 2 S_{Lc}$$

then the analytical method has sufficient accuracy. Otherwise, it is not considered to be as accurate as the laboratories accepted in the certification program.

Values of A_c for KC-1a are presented as the "overall mean" in Table 4 and values of between-laboratories standard deviation, S_{Lc}, are reported in Table 7.

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APPENDIX A

CONFIRMATION OF HOMOGENEITY

Table A9 - Confirmation of homogeneity of KC-1a for zinc

Bottle No.	wt % Zn Individual			Mean
12	34.51	34.56	34.59	34.553
58	34.57	34.55	34.52	34.547
106	34.59	34.56	34.57	34.573
150	34.56	34.56	34.48	34.533
196	34.49	34.53	34.54	34.520
242	34.51	34.54	34.55	34.533
288	34.46	34.50	34.52	34.493
334	34.52	34.48	34.51	34.503
380	34.50	34.49	34.51	34.500
426	34.48	34.50	34.47	34.483
472	34.48	34.48	34.46	34.473
518	34.45	34.47	34.46	34.460
564	34.57	34.55	34.57	34.563
610	34.56	34.58	34.54	34.560
656	34.54	34.53	34.54	34.537
			Overall mean is	34.522

Analysis of variance table

Source of variation	Degrees of freedom	Sum of squares	Mean squares
Between sets	14	5.164×10^{-2}	3.689×10^{-3}
Within sets	30	1.653×10^{-2}	5.511×10^{-4}
Total	44	6.818×10^{-2}	

Calculated F statistic = 6.694

F.95(14,30) = 2.037

Null hypothesis of no difference between bottles is rejected for zinc

didate reference material from its intended use provided that its magnitude is acceptable in comparison with the between-laboratory for the element(s) of interest. The between-bottle standard deviation for KC-1a was calculated to be 0.035 and 0.0023% for zinc and silver, respectively. These are acceptable in comparison with the between-laboratories difference calculated from the results of the interlaboratory program. The latter are 0.289 and 0.0057% for zinc and silver, respectively, thereby demonstrating that KC-1a is sufficiently homogeneous for use as a reference material.

CONFIRMATION OF HOMOGENEITY

The homogeneity of KC-1a was assessed by Bondar-Clegg and Company Limited, Ottawa, Ontario, (SSC Contract 035Q.23440-3-9165) by analyzing in triplicate 15 bottles selected from a stock of 686 for zinc and silver. The stock was divided into 14 lots of 46 bottles and a 15th lot of 52 bottles. The code number of the first was selected at random out of the first lot. The code numbers of the remaining bottles selected were given by the code number of the preceding bottle plus 46. The results are shown in Tables A9 and A10.

A one-way analysis of variance technique was used to assess the homogeneity (5). Herein, the ratio of the between-bottle to within-bottle mean square is compared with the F statistic at the 95% level of probability. Some evidence of bottle-to-bottle inhomogeneity was found for both zinc and silver.

Detection of a statistically significant inhomogeneity of KC-1a with respect to zinc and silver does not necessarily imply that this inhomogeneity is physically significant; experimental difficulties could cause erroneous results. Moreover, a detectable inhomogeneity, statistical, physical or both, also does not disqualify a can-

Table A10 - Confirmation of homogeneity of KC-1a for silver

Bottle No.	wt % Ag Individual			Mean
12	.162	.162	.161	.1617
58	.158	.157	.158	.1577
106	.157	.157	.156	.1567
150	.153	.153	.155	.1537
196	.153	.160	.154	.1557
242	.153	.153	.153	.1530
288	.152	.154	.152	.1527
334	.158	.157	.162	.1590
380	.156	.157	.157	.1567
426	.156	.157	.157	.1567
472	.156	.156	.154	.1553
518	.155	.154	.154	.1543
564	.155	.154	.155	.1547
610	.156	.156	.156	.1563
656	.157	.156	.156	.1560
			Overall mean is	.1560

Analysis of variance table

Source of variation	Degrees of freedom	Sum of squares	Mean squares
Between sets	14	2.280×10^{-4}	1.629×10^{-5}
Within sets	30	5.600×10^{-5}	1.867×10^{-6}
Total	44	2.840×10^{-4}	

Calculated F statistic = 8.724

F.95(14,30) = 2.037

Null hypothesis of no difference between bottles is rejected for silver

APPENDIX B

PARTICIPATING LABORATOIRES

PARTICIPATING LABORATORIES

Assayers (Ontario) Ltd.
Toronto, Ontario
J. van Engelen

Atlantic Analytical Services Ltd.
Saint John, New Brunswick
W. Wilson

Bondar-Clegg and Company Ltd.
North Vancouver, British Columbia
R.K. Rogers

Bondar-Clegg and Company Ltd.
Ottawa, Ontario
P. Haulena

CANMET, Mineral Sciences Laboratories
Energy, Mines and Resources Canada
Ottawa, Ontario

CANTEST Ltd.
Vancouver, British Columbia
R.S. Jornitz

Chemex Labs Alberta Ltd.
Calgary, Alberta
R.B. Pang

Chemex Labs Ltd.
North Vancouver, British Columbia
B.L. Twaites

Falconbridge Nickel Mines Ltd.
Metallurgical Laboratories
Thornhill, Ontario
J.R. Johnston

Hudson Bay Mining and Smelting Company Ltd.
Flin Flon, Manitoba
D. Allen

Kamloops Research and Assay Laboratory Ltd.
Kamloops, British Columbia
D. Blundell

Kidd Creek Mines Ltd.
Timmins, Ontario
J.M. Labreque

Lakefield Research of Canada Ltd.
Lakefield, Ontario
D.M. Wyslouzil

Metriclab (1980) Inc.
Ste-Marthe-sur-le-Lac, Quebec
H. Blais

MINTEK
Randburg, South Africa
E.J. Ring

Noranda Research Centre
Pointe Claire, Quebec
J.D. Kerbyson

Ontario Ministry of Natural Resources
Geoscience Laboratories
Toronto, Ontario
C. Riddle

Technical Services Laboratories
Mississauga, Ontario
A.H. Debnam

X-ray Assay Laboratories Ltd.
Don-Mills, Ontario
E.J. Brooker